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Lithium-Aluminate-Catalyzed Hydrophosphination Applications

Victoria A. Pollard, Allan Young, Ross McLellan, Alan R. Kennedy, Tell Tuttle, and Robert E. Mulvey*

Abstract: Synthesized, isolated, and characterized by X-ray crystallography and NMR spectroscopic studies, lithium phosphidoaluminate IBuAlPPh$_3$Li(THF)$_3$ has been tested as a catalyst for hydrophosphination of alkynes, alkenes, and carbodiimides. Based on the collective evidence of stoichiometric reactions, NMR monitoring studies, kinetic analysis, and DFT calculations, a mechanism involving deprotonation, alkyne insertion and protonolysis is proposed for the [IBuAlHILi$_2$], aluminate-catalyzed hydrophosphination of alkynes with diphenylphosphine. This study enhances further the development of transition metal free, atom economical homogeneous catalysis using common sustainable main group metals.

Introduction

Phosphines are utilized in a range of applications spanning agriculture, medicinal chemistry, and organocatalysis, while their ubiquity as ligands in transition metal catalysis is legend.\[1]\[5\] Hydrophosphination, adding a P–H bond across an unsaturated C–E (E = e.g., C, N) bond, offers atom economy to preparing phosphines.\[5\] Many transition (e.g., based on Fe, Ni, Pd and Zr)\[2b, 2c, 3a, 3b\] and rare earth (e.g., La, Sm, and Yb)\[3\] metal catalysts have been used for hydrophosphination, while solvent and catalyst-free hydrophosphinations can also be thermally induced under certain circumstances.\[4\] Developing catalysts based on main group metals is currently trending in homogeneous catalysis including hydrophosphination.\[5\] K, Ca and Mg complexes have been reported as hydrophosphination catalysts for alkene, alkyne and carbodiimide substrates with diphenylphosphate (HPPh$_2$), forming alkyl phosphines, vinyl phosphines and phosphaqueunaines, respectively.\[3a, 3b, 6\] Tin complexes are also capable of catalysing hydrophosphination reactions,\[2c, 7\] though Cp*$_2$SnCl$_2$ (Cp* = pentamethylcyclopentadienyl) required an H$_2$ atmosphere to inhibit competing phosphate dehydrocoupling of HPPh$_2$.\[7b, 8\]

Attractive industrially due to its high natural abundance and low toxicity, aluminium is gaining prominence in this main group catalysis enlightenment.\[9\] Work by Roesky, Wright, Cowley/Thomas, Harder, Stephan, and others, have successfully employed Al-based catalysts in hydroboration and hydrogenation.\[10\] Uhl has also demonstrated that a P/Al geminal FLP can stoichiometrically hydrophosphinate heteroatom substituted nitriles, generating imines incorporated into 5-atom AlCPPCN heterocycles.\[11\] Examples also exist of Al-catalyzed hydrophosphonylation (using P(V) reagents)\[12\] However, to our knowledge no examples exist of Al-catalyzed hydrophosphination (using P(III) reagents) of alkynes, alkenes or carbodiimides.

Bimetallic aste complexes, which can synergistically enhance stoichiometric reactivities over their neutral monometallic components, are a core theme of our research.\[13\] Recently expanding this work into the catalytic regime, we used lithium aluminates as catalysts for hydroboration of aldehydes, ketones, imines and acetylens.\[14\] In general, the charged bimetallic species proved more active catalysts than their neutral monometallic components.\[14\] Here, we probe the ability of our most active lithium aluminate, [IBuAlHILi]$_2$, 1, as a catalyst for hydrophosphinylation of alkynes, alkenes, and carbodiimides.

Results and Discussion

First, we reacted phenylacetylene with HPPh$_2$ and 10 mol% of dimeric [IBuAlHILi]$_2$ in C$_6$D$_6$ at 70 °C. This reaction gave a very low 5% conversion after 20 h and it was proposed a higher boiling point solvent would be required to allow the catalysis to proceed. Moving to d$_5$-toluene at 110 °C yielded 72% conversion (1:8 E/Z ratio, Fig. 1) within 20 h, to the anti-Markovnikov product consistent with syn addition of H–P across the C=C bond. Changing the solvent to polar d$_5$-THF (65 °C) lowered the E/Z selectivity to 1:3. We propose that in d$_5$-THF solution the resulting lithium aluminium phosphide (vide infra) exists in an equilibrium, as observed by the presence of three separate distinct signals for the iso-butyl ligands in the $^1$H NMR spectrum. Using CD$_2$Cl$_2$ (40 °C) poisoned the catalyst giving no product. Satisfied this system is a capable hydrophosphination catalyst, a range of alkynes were screened (Table 1). Internal alkynes, diphenylacetylene and 1-phenyl-1-propyne reacted faster than terminal alkynes. However, more challenging unactivated alkynes, 1-hexyne and 3-hexyne did not react, in common with other reports of main group catalysed hydrophosphination.\[7b\]

To gain more insight, a 1:1:3 stoichiometric reaction between [IBuAlHILi]$_2$, HPPh$_2$, and THF, completely consumed the aluminate giving a solution that deposited crystals of the lithium aluminium phosphide, IBuAlPPh$_3$Li(THF)$_3$, 2, (isolated yield, 41%) (Fig. 1a). Phosphidoaluminate 2 results from deprotonation of HPPh$_2$.
by 1, and importantly, implies this process is the first step in catalytic hydrophosphination. Crystalline 2 (Fig. 1b) is monomeric, with three THF molecules solvating Li. $^1$H DOSY NMR studies confirm it remains monomeric in $d_8$-toluene solution.$^{[15]}$ Alternatively, 2 can be made by co-complexing LiPPh$_2$ with iBu$_2$Al/THF.

Aware that dehydrocoupling can compete with hydrophosphination, a control reaction between HPPH$_2$ and 10 mol% of 2 in $d_8$-toluene was heated at 110 °C for 20 h. Less than 15% of HPPH$_2$ had undergone dehydrocoupling to form 1,1,2,2-tetraphenyl diphosphine (determined by $^{31}$P NMR spectra) signifying that this is unlikely to be a significant problem in this system. Subsequently 2 was tested as a catalyst for hydrophosphination of alkynes, under the previously optimised conditions (10 mol% [Al], $d_8$-toluene, 110 °C), (Table 1). For phenylacetylene a 95% conversion (1:3 $E$/Z ratio) of the anti-Markownikov product was obtained after 20 h (cf. 72% using 1), albeit with reduced $E$/Z stereoselectivity. By contrast, Waterman’s tin catalyst Cp$_3$SnCl$_2$ is poorly active for PhC≡CH (10 mol% catalyst, 18 h, 65 °C, 4% yield).$^{[50]}$ Using 2, hydrophosphination is much faster with internal alkynes than terminal alkynes, with a 99% yield (10:1 $E$/Z ratio) for diphenylacetylene being obtained within just 1 h (1 takes 5 hours). Similarly, 1-phenyl-1-propyne fully converts to the anti-Markonikov vinyl phosphate product within 1 h. The catalytic activity of 2 with PhC≡CPh compares favourably with the $\beta$-diketiminate calcium amide catalyst DIPP[NacNacCa(HMDS)](THF), which required extended reaction times (10 mol% catalyst, 75 °C, 13 h, 94% yield).$^{[6c]}$ However, [Ca(PPh$_3$)$_2$(THF)$_4$] catalytically hydrophosphinated diphenylacetylene after 2 h at room temperature.$^{[6d]}$ Cui used an imino-amidinate ligated Ca catalyst for quantitative hydrophosphination of 1-phenyl-1-propyne after 5 h at 60 °C, using 5 mol% [Ca].$^{[36]}

Adding a catalytic amount (30 mol%) of THF to 10 mol% of 1 resulted in hydrophosphination of diphenylacetylene within the same time as that using pre-formed 2, suggesting that deaggregation of dimeric 1 by THF is advantageous in catalysis. Again attempted catalysis with unactivated 1-hexyne or 3-hexyne and HPPH$_2$ by 2 proved unsuccessful. Deaggregation aside, the coordination shell surrounding a metal cation can play a key role in modulating the Lewis acidity of the metal, thereby providing a potential route to modify reactivity. Thus, we explored the effect of the Lewis donor on hydrophosphination of PhC≡CPh. A range of Lewis donor additives were added to the hydrophosphination reactions of diphenylacetylene catalysed by 1. Adding either two equivalents (with respect to the catalyst) of bidentate donor TMEDA (N,N,N’,N’-tetramethylethylenediamine) or one equivalent of 12-crown-4 result in quantitative conversions in 1 h, the same time as when 3 equivalents of THF are used. The molecular structure of the organometallic compound in the presence of polydentate 12-crown-4 was determined via X-ray crystallography as the contacted ion pair structure, iBu$_2$AlPPh$_2$Li(12-crown-4), with the phosphorus atom bridging the Al and Li centres (see ESI). Unfortunately, due to poor quality data no geometric parameters can be discussed, however the structure provides unequivocal proof of atomic connectivity. The use of isolated iBu$_2$AlLi(PMDETA) also results in quantitative product formation within 1 h (tridendate PMDETA = N,N,N’,N’-pentamethyldiethylenetriamine). This complex was crystallographically characterised (Fig. 2), but all organic ligands exhibit significant disorder which precludes a discussion of geometric parameters beyond atomic connectivity.

![Figure 1. a) Synthesis of iBu$_2$AlPPh$_2$Li(THF)$_2$. b) Molecular structure of 2. H atoms and disordered THF molecules omitted for clarity, thermal ellipsoids drawn at 40% probability; c) Depiction of $E$, $Z$-stereoisomers and $\alpha$-regioisomers arising from hydrophosphination of alkylene substrates.](image-url)
Interestingly, the E/Z-isomer ratio is dependent on the donor used. PMDETA and 12-crown-4 are less selective (E/Z 2:1; and 5:1 respectively, versus 10:1 with 3 THF), whereas 2 TMEDA donors result in enhanced E/Z-selectivity of 19:1. Adding one equivalent of bulky tetradoentate Me₆-TREN, takes 3 h for quantitative conversion (E/Z 10:1). Adding two equivalents of bidentate dppe (diphenylphosphinoethane) results in conversion in 5 hours, albeit with good E/Z selectivity (16:1). Interestingly it appears that when two bidentate donors are added, TMEDA or dppe, marked improvements in selectivity occur. Finally, adding three equivalents of PPh₃ to preformed 2 results in both slower catalysis (1.5 h) and poorer selectivity (E/Z 4:1) than those observed with the THF variant, indicating the phosphine Lewis donor may inhibit the hydrophosphination process.

Next, the more challenging hydrophosphination of alkynes was examined using 2 (Table 1). Styrene undergoes hydrophosphination in 6 h, at 110 °C, yielding 84% of the anti-Markovnikov product. Halo-substituted styrenes are also tolerated (Table 1, entries e-f). 4-Vinyl anisole undergoes hydrophosphination to the alkyl phosphate product in 87% yield after 20 h at 110 °C. Bulkier substrates such as α-methyl styrene, trans-β-methyl styrene, and the less activated alkene 1-hexene did not undergo hydrophosphination with 2 as the catalyst. Similar failures with both Ca and Sn based catalysts have been noted for these substrates.¹⁶ Hydrophosphination of vinyl boronic acid pinacol ester (vinyl Bpin) achieved a 93% yield after 4 h at 110 °C, producing linear phosphate boronic ester Ph₂P(CH₂)₃Bpin. To our knowledge this is the first time Ph₂P(CH₂)₃Bpin has been made via a hydrophosphination route, since earlier published methods required hydroboration of diphenyl vinyl phosphate.¹¹⁶

Table 1. Hydrophosphination of alkynes, alkenes and carbodiimides using 1 – 6 as catalysts.

<table>
<thead>
<tr>
<th>Alkynes³²</th>
<th>Alkenes³²</th>
<th>Carbodiimides³²</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) <img src="image.png" alt="Image" /></td>
<td>b) <img src="image.png" alt="Image" /></td>
<td>c) <img src="image.png" alt="Image" /></td>
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<td><img src="image.png" alt="Image" /></td>
</tr>
<tr>
<td>Catalyst; yield (%); E/Z/α-isomer ratio; time (h)</td>
<td>1 72%, 1:8:0, 20 h</td>
<td>1 98%, 1:10:1, 5 h</td>
</tr>
<tr>
<td></td>
<td>2 95% (78%), 1:3:0, 20 h</td>
<td>2 99% (82%), 10:1, 1 h</td>
</tr>
<tr>
<td></td>
<td>3 86%, 1:3:0, 20 h</td>
<td>3 98%, 10:3, 3 h</td>
</tr>
<tr>
<td></td>
<td>4 72%, 1:8:8, 20 h</td>
<td>4 72%, 1:8:8, 20 h</td>
</tr>
<tr>
<td></td>
<td>5 62%, 1:12:4, 20 h</td>
<td>5 62%, 1:12:4, 20 h</td>
</tr>
<tr>
<td></td>
<td>6 62%, 1:12:4, 20 h</td>
<td>6 62%, 1:12:4, 20 h</td>
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General conditions: 0.6 mmol substrate, 0.5 mmol HPPh₃, di-toluene. Conversions based against ¹H NMR internal standard hexamethyldicyclohexylsiloxane. E/Z/α stereoselectivity based on ³¹P NMR spectra. Selected isolated yields in parenthesis. [a] [b] 10 mol% [Al] catalyst, 110 °C [c]: 5 mol% [Al] catalyst, RT.

Phosphidoaluminate 2 is also an able catalyst for hydrophosphination of carbodiimides at room temperature. Thus, using 5 mol% catalyst loading (Table 1, entries i-j), disopropylcarbodiimide is converted fully to the phosphaguanidine product within 15 minutes; while bulkier dicyclohexylcarbodiimide required 20 h, to achieve 86% conversion. Hill reports quantitative yields for disopropyl– and dicyclohexyl–carbodiimides within 1 h and 4 h,

**Figure 2.** Molecular structure of iBu₂AlLi(PMDETA). Thermal ellipsoids are drawn at 40% probability, and disordered iBu groups, disordered PMDETA, and hydrogen atoms, except hydride, have been removed for clarity.
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Table 2. Effect of Lewis donor upon hydrophosphination catalysis of diphenylacetylene.

<table>
<thead>
<tr>
<th>Lewis donor additive</th>
<th>Time (h)</th>
<th>Yield(%) / (E/Z ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None [Bu₂AlHL₃]₂</td>
<td>1</td>
<td>99 / 2:1</td>
</tr>
<tr>
<td>1 + 3 equiv. THF</td>
<td>2</td>
<td>99 / 10:1</td>
</tr>
<tr>
<td>iBu₂AlH₂(PMDTA)</td>
<td>1</td>
<td>99 / 10:1</td>
</tr>
<tr>
<td>1 + 1 equiv. 12-crown-4</td>
<td>1</td>
<td>99 / 5 : 1</td>
</tr>
<tr>
<td>1 + 2 equiv. TMEDA</td>
<td>1</td>
<td>99 / 19:1</td>
</tr>
<tr>
<td>1 + 1 equiv. Me₃TREN</td>
<td>3</td>
<td>95 / 10:1</td>
</tr>
<tr>
<td>1 + 2 equiv. dppe</td>
<td>5</td>
<td>95 / 16:1</td>
</tr>
<tr>
<td>iBuAlPPPh₂Li[(THF)₃]</td>
<td>1</td>
<td>99 / 10:1</td>
</tr>
<tr>
<td>2 + 3 equiv. PPh₃</td>
<td>1.5</td>
<td>99 / 4:1</td>
</tr>
</tbody>
</table>

General conditions: 0.6 mmol substrate, 0.5 mmol HPPh₂, d₅-toluene, 10 mol% [Al] catalyst, 110 °C. Conversions based on 1H NMR internal standard hexamethyldisiloxane. E/Z α stereoselectivity based on 31P NMR spectra.

respectively, using 2 mol% Ca(HMDS)₂ as catalyst, also at room temperature. Significantly longer reaction times were seen when using [AlPPh₂]₂ as a catalyst (1.5 mol%) (iPr, 6 h, 99%: Cy, 28 h, 85%).[6d] KHMD is also found to be a good catalyst for carbodiimides requiring lower catalyst loadings and short reaction times,[6a] while a sodium magnesiate also catalyses hydrophosphination of carbodiimides.[6b]

Attempting to pinpoint the active catalyst, four compounds LiPPh₂ (3), iBu₃Al (4), iBu₂AlH (5) and iBu₂AlPPh₂ (6),[15] were screened for catalytic viability using PhC≡CH as a model substrate (Table 1). Using LiPPh₂ as a catalyst yields 86% conversion to the vinyl phosphine after 20 h, with anti-Markovnikov regioselectivity, similar to that of 2. Compounds 4-6 afford different product regio- and stereo-selectivities as well as lower yields for PhC≡CH hydrophosphination. Interestingly when 4 is used as catalyst (72%); 1:8:8 E/Z/α the major isomer products are the Z- anti-Markovnikov isomer, and equally the Markovnikov [α – isomer; Ph(PH₃)₂C=CH₂]. In contrast, 2 does not give any appreciable α-isomer, suggesting 2 is not disproportionate in solution at high temperature into LiPPh₂ and iBu₃Al. In order to ascertain whether LiPPh₂ is implicated in the catalytic profile we conducted another stoichiometric reaction (see ESI). Monitoring reaction of 2 and PhC≡CPh, in d₅-toluene, by 31P NMR shows that after 2 h at 110 °C full consumption of 2 occurs with concomitant growth of two new signals at 3.4 and -15.5 ppm. Unable to isolate these species despite several attempts, we tentatively assign them as two isomers resulting from insertion of diphenylacetylene into 2. Subsequent addition of HPPH₂ and further heating at 110 °C allows for product formation [8.9 ppm (E-isomer) and -7.3 ppm (Z-isomer)] and regeneration of 2 (-49.3 ppm).

We rationalise the intermediate (at 3.4 ppm) reacts onwards to form the E-stereoisomer as it is consumed faster than the other intermediate. Significantly there are no resonances corresponding to LiPPh₂ in the spectrum (-52 ppm) further reinforcing the view that 2 is the catalytically active species. We propose a catalytic cycle (Scheme 1) that begins by deprotonation of HPPH₂ by [iBu₂AlHL]₂, releasing H₂ and forming compound 2. Next, a substrate molecule inserts into the Al–P bond. Subsequent protonolysis by a second equivalent of HPPH₂ accesses the hydrophosphinated product whilst regenerating the active catalytic species 2.

Since after the facile room temperature deprotonation step, alkyne insertion and protonolysis are the other key steps, we performed a deuterium labelling study to investigate the cycle further. Catalytic hydrophosphination between PhC≡CPh and DPPH₂ favoured formation of the E-stereoisomer and deuterium was incorporated into the vinyl phosphine product, Ph(Ph₃)P≡C(D)Ph, as confirmed by 2H NMR spectra and GC-MS (see ESI). Also, in a stoichiometric reaction between [iBu₂AlHL]₂ and DPPH₂, HD was detected in the 1H NMR spectrum (triplet at 4.45 ppm, J = 42.8 Hz), confirming the initial deprotonation step.

A kinetic isotope effect experiment (KIE) was conducted for hydrophosphination of diphenylacetylene by recording the reaction profile in duplicate for HPPH₂ and DPPH₂ at 100 °C, in d₅-toluene, with 10 mol% of 2. By monitoring the consumption rate of phosphine by 31P NMR, rates were obtained, and in each case the overall reaction rate is pseudo-first order. From these rates a KIE of 1.38 ± 0.13 was determined (see ESI). This is a small value, compared with other literature reports, and suggest that cleavage of the...
P–H bond is only involved to a minor extent in the rate determining step.\textsuperscript{[26]} This also indicates that alkyne insertion into 2 is rate determining, which given the rather congested structure of 2 and bulky nature of the alkyne is unsurprising.

Next, we conducted a kinetic analysis of the reaction using the Variable Time Normalisation Analysis (VTNA) method reported by Burés, allowing us to obtain valuable mechanistic detail under synthetically relevant conditions to three half-lives (see Fig. 3 and ESI).\textsuperscript{[14]} The reaction order with respect to [catalyst] was determined by conducting reactions using different catalyst concentrations, while keeping [alkyne] and [phosphine] constant. These data showed the reaction rate increases with increasing [catalyst], and that the order in catalyst is 1. This situation is consistent with the reaction proceeding via a monomeric rate determining step during the reaction. Variation of [phosphine] under synthetically relevant conditions revealed that increasing concentration of phosphine inhibits the reaction, giving a phosphine order of -1. This inhibition likely results from pre-coordination of the phosphine, blocking off the alkyne for insertion. Also, we have already established that bulky mono- and bidentate phosphines slow down reactivity in our Lewis donor study (vide supra). Lastly, variation of [alkyne] revealed a first order dependence in [alkyne], indicating that the alkyne is involved in the rate limiting step.

Finally, in order to reinforce our experimental insight, we turned to DFT calculations. Run on the full system with the internal alkyne, diphenylacetylene, used as the model substrate, the calculations were performed at the B3LYP-D3\textsuperscript{[19]} 6-311G(d,p)\textsuperscript{[20]} level of theory employing a continuum solvent with the dielectric constant of toluene within the IEFPCM model.\textsuperscript{[21]} The relative stability of the formation of 2 from [Bu₃AlH][AlEt₃]₂ with 2 HPPh₂ and 6 THF molecules was initially investigated. Formation of the catalyst (2) is thermodynamically favourable despite the entropic penalty associated with THF coordination, with a calculated ∆G = -63.8 kcal/mol (ΔH = -130.8 kcal/mol). The activation barrier for the formation of the catalyst was challenging to isolate as a result of the complex potential energy surface associated with the large dimer species. However, a bond scan along the coordinate associated with the formation of H₂ provided an indicative barrier (∆E*) of ~38 kcal/mol, which would be achievable under the reaction conditions and lead irreversibly to 2 given the exothermic nature of this step. In contrast to the induction step, the first step in the catalytic cycle (adding diphenylacetylene to 2) is mildly endergonic for both the E and Z isomers of the intermediate shown in Scheme 1. However, the E isomer is more stable in the intermediate state of the reaction (∆G = 6.9 kcal/mol), with the Z-isomer (∆G = 8.3 kcal/mol) being further destabilised by 1.4 kcal/mol, relative to the E-isomer. Finally, generation of the product and reformation of the catalytic species occurs in an exergonic reaction. In this step, the formation of the Z-isomer (∆G = -25.3 kcal/mol) is favoured over the E-isomer (∆G = -20.4 kcal/mol). The reversal of the relative stabilities of the isomers in the intermediate state versus the product state suggests that the formation of the intermediate is deterministic for the final product distribution, which favours the experimentally determined E-isomer. The rate-limiting step for the reaction could not be located as the calculation of transition states proved elusive for these bulky compounds. However, the relative stabilities of the intermediates and products determined for this pathway indicate that the mechanism proposed is achievable under the reaction conditions employed.

**Conclusion**

Previously lithium aluminates have been shown to be active catalysts for hydroboration of aldehydes, ketones, imines and acetylenes. This new study extends the catalytic chemistry of these bimetallic main group compounds by reporting the first example of Al-catalysed hydrophosphination of alkenes, alkenes

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**Figure 3.** Variable Time Normalisation Analysis (VTNA) plots illustrating the order in a) catalyst (first order); b) phosphine (inverse first order); c) diphenylacetylene (first order).
and carbodiimides, using the lithium aluminate (pre)catalyst [iBuAlH][Li]. A mechanism is proposed for the alkynyl catalysis, elucidated by stoichiometric reactions, thought to proceed via formation of the crystallographically defined lithium aluminium phosphide, [iBuAlH][Li][THF], 2, followed by insertion of the alkynyl into the Al-P bond, then protonolysis of a secondary equivalent of the phosphine to generate the vinylphosphine product and regenerate the catalyst. While intuitively the formation of an anionic aluminium centre saturated by four anionic ligands as in an aluminate might be expected to have insufficient Lewis acidity to engage in hydrophosphination processes, it is clear from the different results obtained using a number of Lewis donor solvent molecules that the presence of the lithium helps to circumvent this apparent handicap so pointing to bimetallic synergistic behaviour.

**Experimental Section**

Full experimental characterisation and synthetic procedures are described in the supporting information.

**Synthesis of iBuAlHPPPh2Li[THF], 2:** method a) To a stirred solution of [iBuAlH][Li] (0.412 g; 1 mmol) in hexane (10 mL) was added HPPPh2 (0.34 mL; 2 mmol) and the reaction stirred 1 h. THF (0.5 mL; 6 mmol) was added then the volatiles were removed. The residue was taken up in hexane (5 mL) and toluene (1 mL). Subsequent cooling to −30 °C yielded the desired product as pale-yellow crystals. Crystalline yield 0.494 g; 74 %. method b) To a stirred solution of HPPPh2 (0.17 mL; 1 mmol) in hexane (5 mL) was added dropwise nBuLi (0.63 mL; 1.6 m M; 4.1 mmol), the mixture stirred 10 min and the reaction was regularly monitored by 0.09 NMR tube and the reaction was regularly monitored by

**General Catalytic Reaction:** The desired catalyst loading was added to 0.5 mL of d8-toluene solution (unless alternative solvent specified) containing the substrate precursor (0.6 mmol) and HPPPh2 (0.5 mmol, 0.09 mL). The reaction mixture was transferred to a sealed J. Young’s tap NMR tube and the reaction was regularly monitored by 1H and 31P NMR spectroscopy until the formation of the products was completed as determined by integration versus an internal capillary standard (hexamethyldisiloxane). For alkynes and alkenes, the hydrophosphination catalysis was performed at 110 °C with 10 mol% [Al] catalyst loading. For carbodiimides the hydrophosphinination catalysis was performed at room temperature with 5 mol% [Al] catalyst loading. The yields reported are based on 1H NMR and 31P relative to the internal standard. In all cases, the bulk of the NMR solution can be attributed to either product compounds or starting materials. Isolated yields are provided for example substrates, isolated via either recrystallization methods or column chromatography, as reported in the ESI.

**Acknowledgements**

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**Keywords:** Aluminate • Homogeneous Catalysis • Hydrophosphinination • Lithium • Phosphine

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Alluring Aluminium: catalytic hydrophosphination of unsaturated organic substrates is usually associated with transition metals, but here aluminium is found to be an attractive catalytic partner.